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POTENTIOMETRIC MEASUREMENT OF SODIUM CHLORIDE IN CHEESE

by

Seyed-Hossein Salimi

A thesis submitted in partial fulfillment  
of the requirements for the degree

of

MASTER OF SCIENCE

in

Dairy Science

UTAH STATE UNIVERSITY ♦  
Logan, Utah

1966

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I am also grateful to Mahshid for her encouragement and taking care of our daughter, Salma.

This thesis is dedicated to my father Seyed-Aziz Salimi who made my studies in the United States possible.

Seyed-Hosseini Salimi

# TABLE OF CONTENTS

|   |    |
|---|----|
| INTRODUCTION . . . . .  | 1  |
| REVIEW OF LITERATURE . . . . .  | 2  |
| Determination of salt in dairy products . . . . .                             | 2  |
| Development of sodium ion electrodes . . . . .                                | 4  |
| Theory of potentiometric measurement of ion activity . . . . .                | 7  |
| MATERIALS AND METHODS . . . . .   | 9  |
| Water . . . . .   | 9  |
| Potentiometer . . . . .   | 9  |
| Electrode assembly . . . . .  | 9  |
| Standard sodium chloride solutions . . . . .                                  | 9  |
| Preparation of cheese samples . . . . .                                       | 11 |
| Standard salt analysis . . . . .  | 11 |
| EXPERIMENTAL RESULTS . . . . .  | 12 |
| Standard curve . . . . .  | 12 |
| Effect of pH on response of electrodes to sodium ions . . . . .               | 16 |
| Effect of temperature on values obtained with sodium ion electrodes . . . . . | 17 |
| Cheese analysis . . . . .   | 19 |
| Analysis of commercial salt . . . . .   | 22 |
| DISCUSSION . . . . .  | 24 |
| LITERATURE CITED . . . . .  | 27 |
| APPENDIX . . . . .  | 29 |

# LIST OF FIGURES

| Figure   | Page |
|--|------|
| 1. Equipment for potentiometric measurement of salt in cheese. Osterizer blender, expanded scale pH meter with sodium ion electrode, Frit junction reference electrode and demineralizer . . . . . | 10   |
| 2. Typical calibration curve, drawn on semi-logarithmic graph paper, where sodium ion concentration (M) vs EMF (mv) . . . . .  | 13   |
| 3. Sodium ion concentration (M) vs EMF (mv) as determined with two Na <sup>+</sup> electrodes . . . . .  | 15   |

# LIST OF TABLES

| Table  | Page |
|--|------|
| 1. Effect of pH on potentiometric readings and corresponding concentrations obtained with a $\text{Na}^+$ electrode in standard NaCl solutions . . . . . | 17   |
| 2. Effect of temperature on potentiometric readings and corresponding molarities obtained with standard NaCl solutions . . . . .                         | 18   |
| 3. Comparison of potentiometric and ADSA procedure for salt analysis in five different varieties of cheese .   | 22   |
| 4. Comparison of potentiometric and modified ADSA procedures for salt analysis on analytical NaCl and commercial cheese salts . . . . .                  | 23   |
| 5. Per cent NaCl obtained in five varieties of cheese by potentiometric and ADSA procedure for salt analysis .   | 30   |

## INTRODUCTION

The salt content of cheese is usually determined by the American Dairy Science Association (ADSA) (26) procedure. This method is based upon the determination of chloride in the sample, and results are expressed as per cent sodium chloride. The presence of chlorides in cheese other than sodium chloride would introduce error in the results. However, in practice this is not serious except where relatively large amounts of  $\text{CaCl}_2$  are added to the cheese milk.

In determining the  $\text{NaCl}$  in cheese, one would be as justified in basing his results on sodium analysis as on chloride analysis. An exception would be processed cheese where sodium phosphates and sodium citrate are added to the cheese during processing.

In the past, chloride analysis has been easier and simpler to perform than sodium analysis, and thus has been the procedure of choice for salt determinations in most food products.

The recent development of sodium ion electrodes may now open new possibilities for the determination of  $\text{NaCl}$  in cheese and other foods. Sodium ion electrodes can be used with expanded-scale pH meters and are very convenient for the determination of sodium in biological and other substances (13, 23).

The purpose of this study was to investigate the possibility of using a potentiometer with a sodium ion electrode for the determination of  $\text{NaCl}$  in cheese.

## REVIEW OF LITERATURE

Determination of salt in dairy products. The most common laboratory procedure used for the measurement of salt in cheese is a modified Volhard method described in 1937 by a Committee on Cheese Analysis of the American Dairy Science Association (ADSA) (26). This is an indirect procedure in which the sample must be digested in the presence of an excess of standard silver nitrate. The chloride is precipitated as silver chloride during digestion, and the excess  $\text{Ag}^+$  is then back titrated with standard potassium thiocyanate using ferric ammonium sulfate as an indicator (26). A direct chloride titration method for salt analysis in butter was proposed by Sammis (20) for factory practice. This was a modification of the Mohr titration with silver nitrate in which potassium chromate served as an indicator.

Marquardt (15) compared Sammis' technique with the ADSA method for salt determination on a water suspension of cheese. He found that the soluble proteins in concentrations above 0.2 gram per 100 ml of solution introduced an error proportional to the amount of protein in the sample. Cheese which was not completely broken down was tested accurately by the direct titration method which led to his recommendation that the test be used only on cheese less than five days old.

Skelton and Bryant (22) and Weckel (25) found that dichloro-fluorescein gave a sharper endpoint and greater accuracy than



potassium chromate when used as an indicator in the direct titration test for salt in butter.

Cotlove et al. (8) designed an instrument for an accurate, rapid and automatic determination of chloride in biological samples by electrometric titration with silver ions. Nageswararao and Blobel (16) used this instrument for the determination of chloride in milk, and compared it with the ADSA method and with direct titration with  $\text{AgNO}_3$ . They found that reproducibility with electrometric titration was not as good as with the more laborious ADSA method, but better than with direct titration with  $\text{AgNO}_3$ .

Breene and Price (6) used dichlorofluorescein and potassium chromate as argentometric titration of salt in a water extract of Cheddar cheese. They reported that agreement between the ADSA procedure and the direct titration test using chromate as an indicator was not close enough to justify recommending the use of the potassium chromate indicator for the salt analysis in Cheddar cheese. However, they found that the direct titration test was sufficiently accurate for use in factory and warehouse practice when dichlorofluorescein was used as an indicator. Dichlorofluorescein, however, does not give a sharp end-point in colored cheese solutions. Therefore, experience with the titration is needed in order to get accurate results.

In the ADSA procedure difficulty exists due to the fact that silver thiocyanate is less soluble than the silver chloride precipitate. Unless the silver chloride is prevented from interfering during the back titration with thiocyanate, an indistinct end-point

will occur. Silverman et al. (21) modified the ADSA procedure by adding 2 ml of nitrobenzene. They reported that nitrobenzene will effectively coat the silver chloride precipitate, and prevent further participation during titration. This eliminates the need for decantation or filtration prior to titration.

Recently the Ames Company (1) introduced simple devices for approximating total acidity, alkalinity, and chloride in food products. These devices known as Quantabs are activated by removing the end tab from an inert plastic strip. The exposed end of the strip is placed in the test solution. The sensitive element of the instrument fills by capillary action. It absorbs about two drops of the test solution to make a micro-titration. The component being measured colors the vertical column alongside a scale on the instrument. The height of the colored column represents the concentration of the solution. However, this is not a precise test for determination of NaCl in cheese since the accuracy is  $\pm 10\%$  of the true value.

Development of sodium ion electrodes. Since the discovery in 1914 of the hydrogen ion function at glass membranes (10, 12), glass electrodes have been a subject of curiosity.

In 1923 Horovitz and Schiller (12) studied the response of glass electrodes to sodium and potassium ions. In 1934 Lengyel and Blum (13) observed that by adding  $\text{Al}_2\text{O}_3$  or  $\text{B}_2\text{O}_3$  to sodium silicate glasses, electrodes could be made for which the potential became strongly dependent on the concentration of several cations. Their data indicated that sensitivity to cations probably ranked in decreasing order of  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Li}^+$ . These observations suggested that practical

glass electrodes might be developed for measuring sodium ion activity in ionic mixtures and biological fluids.

Eisenman et al. (9) produced sodium aluminum silicate glasses with a very satisfactory sodium function. Their glass containing 18 M % aluminum was about 250 times more sensitive to sodium than potassium ions.

Bower (5) in 1959 used the same glass electrode, but found that it was about equal in sensitivity to sodium and potassium ions. However, he concluded that it was quite satisfactory for measuring sodium in saline solutions, and found that it gave results within 5% of those obtained with the flame photometer. He also reported that agreement between these methods was sufficiently good to justify use of the electrode for most practical purposes. His measurement precision was  $\pm 1$  mv; and it was probable that with a more sensitive measuring device, the divergence between potentiometric and flame results could have been reduced to about  $\pm 1\%$ .

Difficulties in manufacturing electrodes from sodium aluminum silicate glasses led Beckman Laboratories to seek new glasses of high sodium specificity, but with less refractory physical properties.

Leonard (14) reported that glass containing lithium aluminum silicate had the desirable properties. Surprisingly, the new glass had very high sodium specificity: as high as 1000 to 1 selectivity for  $\text{Na}^+$  over  $\text{K}^+$ . Therefore, until the  $\text{K}^+$  concentration exceeded that of the sodium ion by a factor of ten, the electrode responded to  $\text{Na}^+$  with the theoretical Nernst slope. Lithium ions competed with sodium to about the same degree as potassium in determining the

electrode potential. None of the alkaline earths (magnesium, calcium, strontium, or barium) had any effect over the commonly encountered range of concentrations. Anions did not influence the electrode response except where their presence suppressed or enhanced sodium ion activity. The electrode did not respond to multivalent ions. However, it was just as specific for  $H^+$  as for any metal cation. As a result, it was necessary to raise the pH of a solution, if the cation function of the glass electrode was to be observed. Taulli (24) used one of these electrodes to make potentiometric determinations of small amounts of sodium ions in acid silica sols, and he reported it was very satisfactory for determination of sodium ion in acid silica sols.

Budd (7) used a Bekman sodium ion glass electrode containing lithium aluminum silicate for the determination of silver ions in solution. He observed that it was even more sensitive to  $Ag^+$  than  $Na^+$ . He also observed that the electrode responded in a Nernstian manner to changes in silver ion concentration in the presence of other ions. Therefore such an electrode could have many practical analytical applications in the area of argentometric determination.

Rechnitz and Brauner (19) used cation sensitive glass electrodes to study the weak complex formed between sodium ions and malic acid in aqueous media. They concluded that the potentiometric method improved the reliability and accuracy of this measurement.

Rechnitz and Zamochinck in 1964 (17, 18) studied the response of cation-sensitive glass electrodes to alkali metal ions in ethanol-water and acetone-water mixtures. They found that the response of

glass electrodes was essentially independent of the solvent for a given concentration and type of solute.

Theory of potentiometric measurement of ion activity. Potentiometric measurements of ion concentrations are based upon the fact that definite differences exist between the energy levels of two different states of the same matter, and that these differences are proportional to the relative populations of the atoms or ions concerned. In the case of electrolytic solutions these differences in energy levels are measured as electrical potentials (4, 11, 14). The Nernst equation of classical thermodynamics expresses this potential for a given concentration of ions relative to a standard state as follows:

$$E_m = E_m^\circ + \frac{2.3 RT}{n F} \log_{10} a_m +$$

$E_m$  = Potential of the solid metal.

$E_m^\circ$  = Standard single electrode potential.

$R$  = Universal gas constant (8.314 joules).

$T$  = Absolute temperature.

$n$  = Number of electrons transferred in the reversible reaction.

$F$  = Faraday constant (96,500 coulombs).

2.3 = Proportionality constant relating natural to common logarithms.

$a_m$  = Activity of the ion.

The equation has been written here in a form used to calculate the potential of a metal in contact with a solution of its ions. It

should be noted that  $E_m$  varies in proportion to the logarithm of  $a_m^+$ , which means that a large change in  $a_m^+$  produces only a small change in  $E_m$  (4, 9, 11, 14). The Nernst equation predicts that if  $n = 1$  and  $T = 25^\circ\text{C}$  (298 K) the potential at the glass membrane will change approximately 59 mv. for each decade or ten fold change in ion concentration (14).

Sodium ion concentration is determined with sodium ion electrodes by measuring the potential developed between the test sample and the special filling solution inside the body of the electrode (3).

## MATERIALS AND METHODS

Water. Preliminary experiments revealed the need for high quality distilled water for all solutions in which sodium ion electrodes were used. The general supply of distilled water available in the laboratory was not satisfactory. Therefore, it was passed through a Crystallab demineralizer containing negatively charged resin before it was used in any of these experiments. All the water used for diluting cheese samples, or preparing other solutions in connection with this study had a conductivity value equivalent to less than 1/2 ppm NaCl.

Potentiometer. Potentiometric measurements were made with a Corning Model 10 pH meter with expanded scale. The scale of the meter ranged from -300 to +300 mv with 0.5 mv subdivisions.

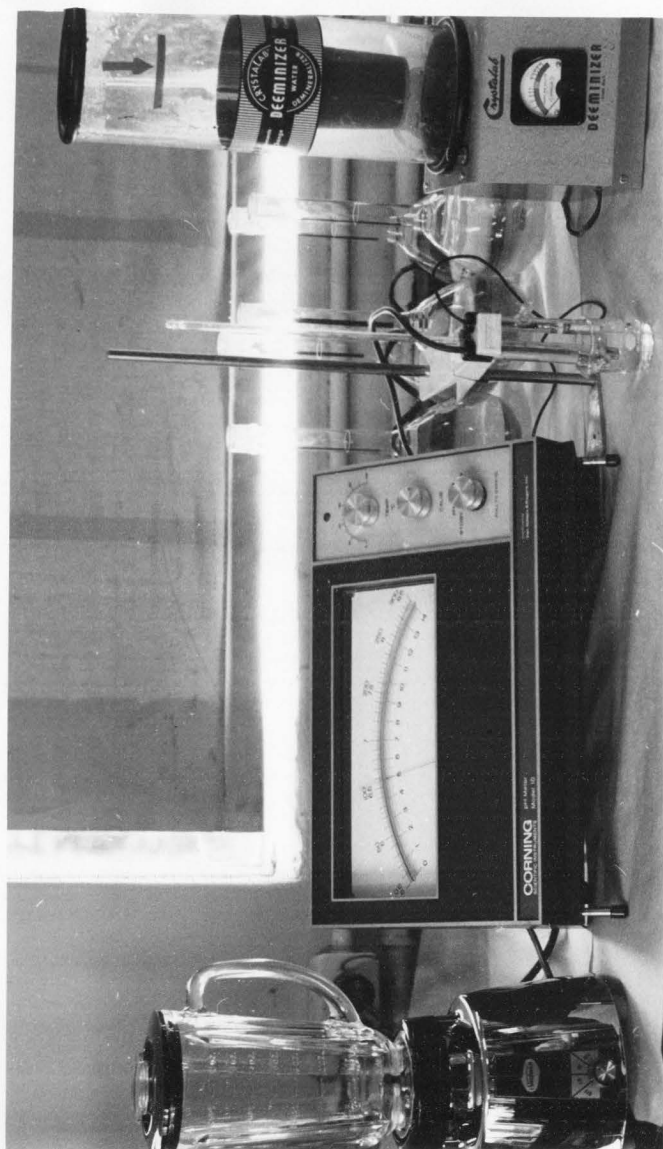
Electrode assembly. Electrodes used in this study were commercially available Beckman No. 39278 sodium ion electrodes (3). These electrodes were made of lithium aluminum silicate glass, and were used with a Beckman No. 39071 frit junction calomel reference electrode. The apparatus used for making potentiometric salt determinations is illustrated in Figure 1.

Standard sodium chloride solutions. Analytical grade NaCl was dried in a vacuum oven for two hours at 120 C, under a vacuum of 27 inches. It was then cooled in a desiccator and used to prepare standard sodium chloride solutions. The pH of each solution was adjusted to 7.5-9.5 by adding solid barium hydroxide.





Figure 1. Equipment for potentiometric measurement of salt in cheese. Osterizer blender, expanded scale pH meter with sodium ion electrode, Frit junction reference electrode and demineralizer.



Preparation of cheese samples. Samples of cheese were pressed through an 8-mesh wire screen and mixed thoroughly in a sample jar. The sample was divided into two portions for separate analysis by the potentiometric and ADSA procedures. Samples were stored in tightly closed containers until analyzed.

Standard salt analysis. The ADSA procedure (26) for the determination of salt in cheese was further modified according to Silverman et al. (21) and used as a standard of comparison for the potentiometric procedure.

Two grams of cheese, 10 ml of 0.1711 N silver nitrate, 10 ml of nitric acid, and 50 ml of water were placed in a 250 ml Erlenmeyer flask. The mixture was boiled, during which time three 5-ml portions of saturated potassium permanganate were added. After the cheese was digested, the clear mixture was cooled and 2 ml of nitrobenzene and 3 ml of ferric ammonium sulfate were added. The flask was shaken and titrated directly with 0.1711 N potassium thiocyanate to a brick-red end-point.

## EXPERIMENTAL RESULTS

Experience with sodium ion electrodes made it clear that reproducible and reliable results depended upon careful preconditioning of the electrodes. Satisfactory results were obtained by soaking the electrodes for 48 hours in a neutral solution of 0.1 M sodium chloride. Electrodes not in use were stored in 0.1 M NaCl. A small polyethylene bottle with a narrow neck which fit tightly around the electrode was a satisfactory storage container, and prevented changes in concentration of the salt during storage.

Changing the concentration of the preconditioning or storage solution changed the response of the electrode to a given concentration of sodium ions.

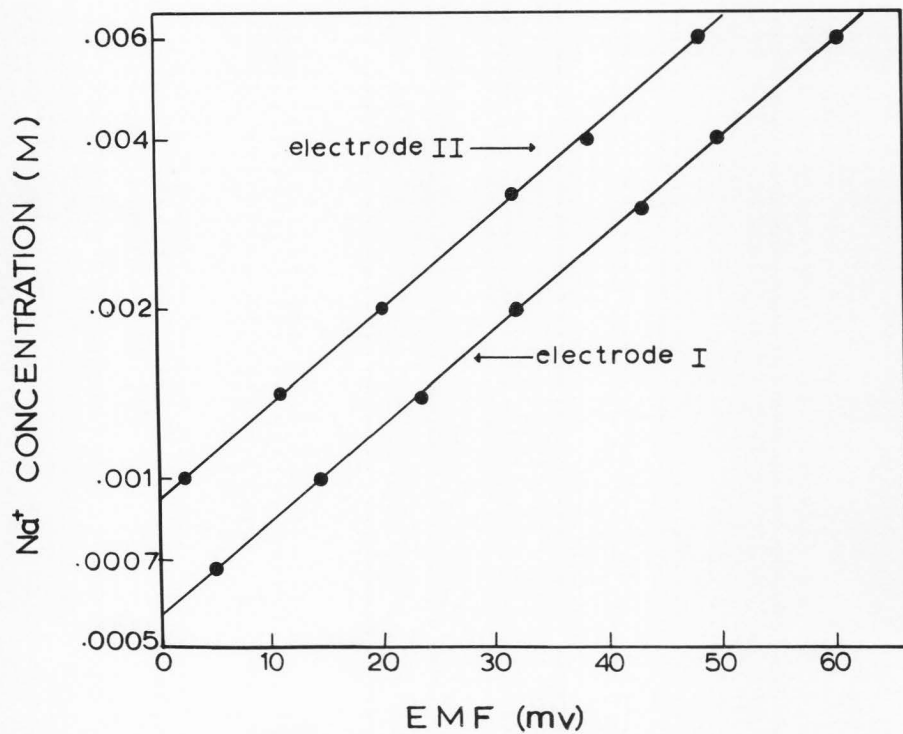
Standard curve. A standard curve was established by plotting EMF (mv) readings against sodium chloride concentration on semi-logarithmic graph paper. A straight line was formed for which the coefficient of correlation was 0.99 (Figure 2). The equation for the standard curve produced with electrode I in Figure 2 was

$$Y = 0.000565 e^{0.039 X}$$

at  $25 \text{ C} \pm 0.5 \text{ C}$ , where Y was the molar sodium ion concentration, e the base for natural logarithms equal to 2.72 and X the EMF value in millivolts. Solutions were kept in 500 ml volumetric flasks covered with parafilm, and were used to check the response of the electrode over a period of several months. All readings over this period remained within  $\pm 0.5 \text{ mv}$ .

- 1991). The authors also found that the frequency of use of the Internet was positively related to the frequency of use of the telephone, and that the frequency of use of the Internet was negatively related to the frequency of use of the television. The authors also found that the frequency of use of the Internet was positively related to the frequency of use of the computer, and that the frequency of use of the Internet was negatively related to the frequency of use of the radio.
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Figure 2. Typical calibration curve, drawn on semi-logarithmic graph paper, where sodium ion concentration (M) vs EMF (mv).



A change of 1 mv in the upper portion of the standard curve (Figure 2) at a concentration of  $3 \times 10^{-3}$  M or 43 mv represents a change of  $1.5 \times 10^{-4}$  M in NaCl concentration, whereas a change of 1 mv at a concentration of  $1.28 \times 10^{-3}$  M or 21 mv represents a change of about  $1 \times 10^{-5}$  M in actual concentration of NaCl. Consequently, all test solutions were diluted to yield readings between 1 and 30 mv. This reduced the effect of errors of measurement on concentration values.

Not all sodium ion electrodes of the type described will give the same millivolt readings at given sodium chloride concentrations. However, the slope of standard curves produced by two different electrodes should be the same if the temperature is constant and the pH is within allowed limits. Figure 3 illustrates two standard curves obtained with two sodium ion electrodes of the same type. Because of the variation in electrodes it was necessary to prepare a standard curve for each electrode. A procedure for preparing a standard curve that covers a range suitable for salt analysis in cheese is given below:

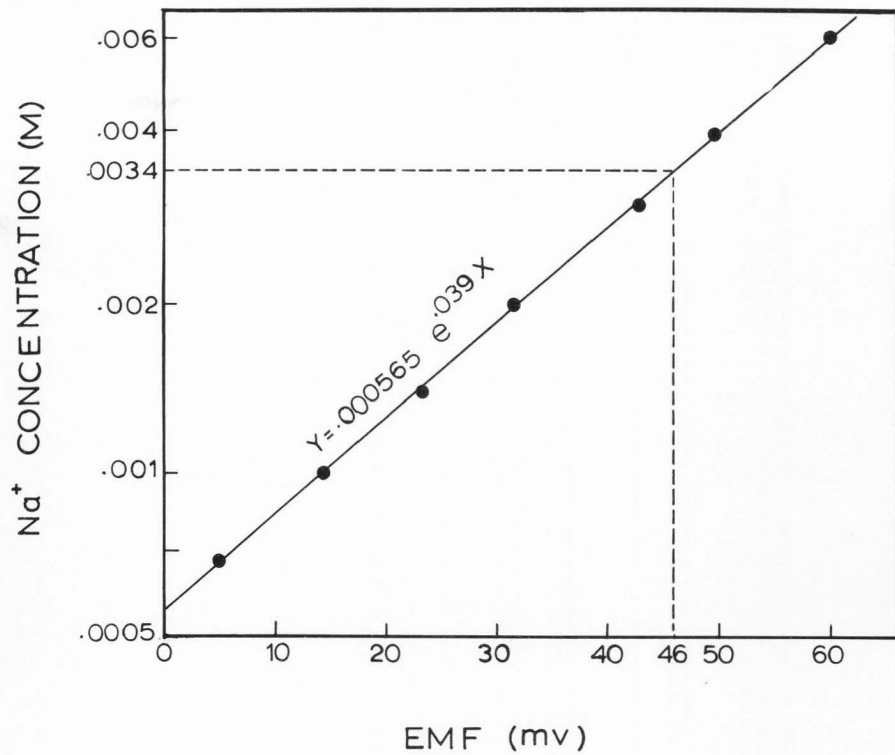
1. Prepare a 0.1 M NaCl solution by weighing 2.9225 grams of previously dried analytical grade NaCl, and transferring it quantitatively to a 500 ml volumetric flask. Dilute to volume and mix well.

2. Make accurate dilutions of the standard solution to concentrations of 0.006, 0.004, 0.003, 0.002, 0.0014, 0.001 and 0.00069 M.



electrons.  
LIVING POLYMERIZATION

Figure 3. Sodium ion concentration (M) vs EMF (mv) as determined with two  $\text{Na}^+$  electrodes.



3. Adjust the pH of the solutions to 7.5-9.5 by adding about 20-30 mg solid barium hydroxide per 500 ml of solution. Then temper to  $25 \pm 0.5$  C in a temperature controlled water bath.

4. Transfer about 30-40 ml of the solution to a 50 ml beaker.

5. Rinse the electrodes with water, dry with tissue and re-rinse with a small amount of the solution to be tested.

6. Immerse the electrodes in the solution about 1 1/2 inches and allow to stand for not less than three minutes.

7. Make sure the temperature is  $25 \pm 0.5$  C, and read the mv value on the expanded scale of the pH meter. Repeat for each solution.

8. Obtain the standard curve by plotting EMF (mv) values against their corresponding concentrations on semi-logarithmic graph paper.

Effect of pH on response of electrodes to sodium ions. Sodium ion electrodes are also sensitive to hydrogen ions. In fact, below pH 4 the hydrogen function becomes predominate and these electrodes perform well as pH electrodes (14). The extent to which pH must be controlled in solutions intended for potentiometric sodium analysis is shown in Table 1. Three solutions containing different known concentrations of sodium chloride were adjusted to pH 6.3, 7.5, 8.5, and 9.5 by adding small amounts of dry barium hydroxide. Potentiometric readings were made on each solution and converted to their corresponding concentration values. These results indicate that pH values from 7.5 to 9.5 had no effect on the performance of the electrode, but that at pH 6.2 a significant deviation occurred in the

potentiometric readings. Therefore for measuring sodium in concentration, it is necessary to raise the pH of test solutions to 7.5-9.5.

Table 1. Effect of pH on potentiometric readings and corresponding concentrations obtained with a  $\text{Na}^+$  electrode in standard NaCl solutions

| pH 6.2        |       | pH 7.5        |       | pH 8.5        |       | pH 9.5        |       |
|---------------|-------|---------------|-------|---------------|-------|---------------|-------|
| Concentration | EMF   | Concentration | EMF   | Concentration | EMF   | Concentration | EMF   |
| (M)           | (+mv) | (M)           | (+mv) | (M)           | (+mv) | (M)           | (+mv) |
| 0.004         | 54.0  | 0.0047        | 50.0  | 0.004         | 50.0  | 0.004         | 50.0  |
| 0.003         | 47.0  | 0.0035        | 43.0  | 0.003         | 43.0  | 0.003         | 43.0  |
| 0.001         | 18.0  | 0.00125       | 14.5  | 0.001         | 14.5  | 0.001         | 14.5  |

Effect of temperature on values obtained with sodium ion electrodes. EMF values on solutions containing 0.004, 0.003 and 0.001 M NaCl were obtained at 22, 25, 26, 28, and 31 C. The results are given in Table 2. As the temperature of the solutions was raised, EMF values also increased. Raising the temperature of the above solutions from 22 C to 25 C, 25 C to 26 C, 26 C to 28 C and 28 C to 31 C resulted in changes of approximately 3, 0.5, 2 and 2 mv respectively. Therefore, it was necessary to adjust all test solutions to the same temperature in order to obtain reproducible results.

Table 2. Effect of temperature on potentiometric readings and corresponding molarities obtained with standard NaCl solutions

| Concen-<br>tration<br>(M) | 22 C         |                           | 25 C         |                           | 26 C         |                           | 28 C         |                           | 31 C         |                           |
|---------------------------|--------------|---------------------------|--------------|---------------------------|--------------|---------------------------|--------------|---------------------------|--------------|---------------------------|
|                           | EMF<br>(+mv) | Concen-<br>tration<br>(M) | EMF<br>(+mv) | Concen-<br>tration<br>(M) | EMF<br>(+mv) | Concen-<br>tration<br>(M) | EMF<br>(+mv) | Concen-<br>tration<br>(M) | EMF<br>(+mv) | Concen-<br>tration<br>(M) |
| 0.004                     | 46.5         | 0.0035                    | 50.0         | 0.004                     | 50.5         | 0.00405                   | 52.5         | 0.0044                    | 54.5         | 0.0047                    |
| 0.003                     | 39.5         | 0.0027                    | 43.0         | 0.003                     | 43.5         | 0.0031                    | 45.5         | 0.0033                    | 48.0         | 0.0037                    |
| 0.001                     | 11.0         | 0.00087                   | 14.5         | 0.001                     | 15.0         | 0.00102                   | 17.0         | 0.0011                    | 18.0         | 0.00125                   |

Cheese analysis. The proposed potentiometric method for the determination of salt in cheese was compared with the conventional modified ADSA procedure on Cheddar and Monterey cheese from Utah State University Dairy Products Laboratory, Blue cheese from Tolibia Cheese Co. Fond du lac, Wisconsin, Swiss cheese from Cache Valley Dairy Association, Smithfield, Utah, and Cottage cheese from Cream O' Weber Dairy, Ogden, Utah.

A 500-1000 gram sample of each hard cheese was ground and pressed through an 8-mesh wire screen and mixed thoroughly in a sample jar. The Cottage and Blue cheese, because of their soft bodies, were blended in an Osterizer blender to a pasty mass. Each cheese was then divided into two lots for salt analysis; one by the potentiometric method and the other by the ADSA procedure.

Salt analyses on each blended cheese were run on 10 to 28 replicates by the potentiometric method and on 10 to 25 replicates by the ADSA procedure. The procedure developed for the potentiometric determination of salt in cheese is given below:

1. Accurately weigh 10.0 grams of previously mixed cheese.

Place it in an Osterizer blender with 200 ml water and blend at high speed for five minutes. Transfer the blended sample to a 1000 ml volumetric flask with several washes, and fill to volume.

2. Shake the volumetric flask thoroughly to produce a uniform cheese suspension, and accurately transfer 10-25 ml of cheese suspension to a 100 ml volumetric flask and fill to volume.

- a. The dilution factor depends upon the percentage salt in the cheese: for Blue cheese, dilute by factor of 5 or 6;

Cheddar and Monterey cheese by factor of 4 or 5; Cottage cheese by 2 or 3; and Swiss cheese by a factor of 1 or 2.

3. Temper cheese solution in a water bath controlled at  $25 \pm 0.5$  C.

4. Shake the flask thoroughly and transfer 30-40 ml of the cheese suspension to a 50 ml beaker.

5. Adjust the pH of the cheese suspension to 7.5-9.5 by adding about 50 mg of solid barium hydroxide ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ).

6. Rinse the electrodes with distilled water and dry with tissue paper. Rinse the electrodes with a small amount of the cheese suspension.

7. Immerse the electrode pair in the beaker to about 1 1/2 inches. Allow to stand for not less than three minutes. Make sure the temperature of cheese solution is at  $25 \pm 0.5$  C before reading the EMF (mv) on the expanded scale of the pH meter.

8. Calculate the per cent NaCl in the cheese by either of following methods:

a. Determine the molarity of the cheese suspension directly from the standard curve (see Figure 2) and compute the percentage salt from formula 1.

$$1. \quad S = 584.5 M D$$

Where S = Percentage salt in the cheese.

M = Molarity from standard curve.

D = Dilution factor

b. Compute the percentage salt from formula 2.



$$2. \quad S = 0.33 D \left[ \text{antilog} (E \times 16.945 \times 10^{-3}) \right]$$

Where S = Percentage salt in the cheese.

D = Dilution factor.

E = mv reading.

Examples of the use of formulas 1 and 2 are given below:

A 10-gram sample of cheese was blended and made to a volume of 1000 ml. It was then diluted four fold, and the EMF of the dilute solution was +10 mv.

Formula 1.  $S = 584.5 M D$

$M = 8.35 \times 10^{-4}$  (obtained from standard curve

Figure 2)

$D = 4$  (dilution factor)

$S = 584.5 \times 8.35 \times 10^{-4} \times 4 = 1.95\% \text{ NaCl in}$

Cheddar cheese

$$\text{Formula 2. } S = 0.33 D \left[ \text{antilog} (E \times 16.945 \times 10^{-3}) \right]$$

$D = 4$

$E = +10 \text{ mv}$

$S = 0.33 \times 4 \times 1.477 = 1.95\% \text{ NaCl in Cheddar}$

cheese

Table 3. Comparison of potentiometric and ADSA procedure for salt analysis in five different varieties of cheese (see Table 5)

| Cheese variety | % NaCl         |         |        |              |         |        |
|----------------|----------------|---------|--------|--------------|---------|--------|
|                | Potentiometric |         |        | ADSA         |         |        |
|                | Replications   | Average | S.D.   | Replications | Average | S.D.   |
| Blue           | 10             | 3.69    | ±0.020 | 10           | 3.76    | ±0.023 |
| Cheddar        | 15             | 1.95    | ±0.028 | 15           | 1.99    | ±0.012 |
| Cottage        | 10             | 1.33    | ±0.012 | 10           | 1.36    | ±0.013 |
| Monterey       | 25             | 1.78    | ±0.022 | 25           | 1.82    | ±0.024 |
| Swiss          | 28             | 0.78    | ±0.035 | 15           | 0.80    | ±0.036 |

Results in Table 3 show that the average values obtained with the potentiometer procedure were slightly lower than those found by chloride analysis. However, the differences were small and standard deviations found for both methods were generally comparable. The potentiometric procedure outlined here seems to be entirely satisfactory for rapid and accurate salt determination in natural cheese.

Analysis of commercial salt. Since the potentiometric salt analysis on all five varieties of cheese gave slightly lower results than the ADSA procedure, an attempt was made to determine whether these differences could be accounted for by differences between pure NaCl and commercial cheese salt. Samples of analytical grade sodium chloride, Diamond Crystal cheese salt and Morton cheese salt were dried for two hours at 120 C, under a vacuum of 27 inches. They were then cooled in a desiccator. A series of solutions was

prepared from each salt which was in turn analyzed by the potentiometric and ADSA procedures. Since there was no organic matter in these salt solutions, dextrose was added to the digestion mixture in the ADSA procedure. This was necessary to destroy the excess potassium permanganate. Results in Table 4 show a very close agreement between the two methods on reagent grade sodium chloride. However, as with the cheese analysis, the potentiometric method gave slightly lower results than the ADSA procedure on samples of commercial cheese salt.

Table 4. Comparison of potentiometric and modified ADSA procedures for salt analysis on analytical NaCl and commercial cheese salts

| Salt            | Known concentration |          | NaCl               |          |
|-----------------|---------------------|----------|--------------------|----------|
|                 | (M)                 | (% NaCl) | Potentiometric (%) | ADSA (%) |
| Analytical NaCl | 0.1                 | 0.5845   | 0.58               | 0.58     |
|                 | 0.086               | 0.5027   | 0.50               | 0.50     |
|                 | 0.043               | 0.2513   | 0.25               | 0.25     |
| Diamond Crystal | 0.006               | 0.0351   | 0.04               | 0.04     |
|                 | 0.004               | 0.0234   | 0.02               | 0.02     |
|                 | 0.002               | 0.0117   | 0.01               | 0.01     |
|                 | 0.001               | 0.0058   | 0.01               | 0.01     |
| Morton          | 0.0855              | 0.4997   | 0.46               | 0.48     |

## DISCUSSION

The sodium ion electrodes used in this study were stable over a period of several months, and gave identical readings on salt solutions of the same concentration. Further work should be done to determine whether electrodes of this type will continue to respond identically over longer periods. However, to avoid error, the electrode should be checked on a standard NaCl solution each time measurements are made.

The sodium chloride content of cheese has an important effect on such quality characteristics as flavor, texture, body and keeping quality. In spite of the critical influence of salt on cheese quality, it is rare that a manufacturer or warehouse operator knows the percentage of salt in the cheese he makes or handles. This may be due in part to the lack of a quick accurate method for analysis of salt in cheese.

Some cheese processors run salt analyses on cheese used for processing. This enables them to accurately standardize the salt content of their finished product. However, present procedures are laborious and time consuming, and frequently encourage guesswork under pressure of busy production schedules.

A common procedure for measuring salt in cheese is described in the AOAC methods of analysis (2). This is a modification of the original Volhard procedure for chlorides (4). A slight modification of the AOAC procedure was described in 1939 by the Committee on

Cheese Analysis of the American Dairy Science Association (26). It is based upon the determination of chloride in the sample, and results are expressed as per cent NaCl. This test requires two standard solutions as well as other toxic chemicals. It also requires digestion of the cheese in a ventilated hood, and titration to an end-point given by a colored indicator.

While chloride analysis has usually been the basis for determining salt in most food products, it is obvious that chlorides other than NaCl would introduce an error. This could occur when  $\text{CaCl}_2$  is added to cheese milk to aid coagulation. The presence of sodium salts other than NaCl could also be raised as an objection to salt determination by sodium analysis. However, the results of this study on five different varieties of natural cheese revealed that salt determinations by potentiometric sodium analysis were just as valid as those made by chloride analysis. However, one could not expect this to be true for processed cheese where sodium phosphate and sodium citrate salts have been added as emulsifiers.

Results of this study indicated that potentiometric sodium analysis gave about 98% of the average salt content obtained by analysis for chloride. However, the same difference was observed when samples of commercial cheese salt were analyzed by the two methods. These findings could have resulted from the presence of small amounts of magnesium or calcium chloride in commercial cheese salt.

Additional work in which the potentiometric method is checked against the flame photometer procedure for sodium would be of benefit

in evaluating the procedure. However, this work has demonstrated that the sodium ion electrode used with an expanded scale pH meter is sufficiently accurate to justify its use for routine salt analysis in cheese.

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## APPENDIX

